

Solution of Ornstein–Zernike Equation for Wall–Particle Distribution Function¹

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The Ornstein–Zernike (OZ) equation is considered for the wall–particle distribution function $g_o(x)$ in the case of a flat, impenetrable wall at $x = 0$ and a fluid of hard-core particles whose centers are constrained by the wall to occupy the semiinfinite space $x > \sigma/2$, where σ is the particle diameter. A solution is given in terms of the wall–particle direct correlation function $c_o(x)$ for $x > \sigma/2$, the bulk–fluid direct correlation function $c_B(t)$, and ρ_B , the average bulk density. Explicit formulas for the contact surface density, total excess surface density, and the Laplace transform of the fluid density near the wall are given. For mean spherical type approximations, $c_o(x)$ for $x > \sigma/2$ and $c_B(t)$ are both prescribed functions; for this case, a closed-form solution is obtained. An example is discussed and additional equations that enable one to go beyond the approximations considered above are introduced.

KEY WORDS: Wall–particle distribution function; Ornstein–Zernike equation; electrode-ion distribution function.

1. INTRODUCTION

Quite recently, Henderson *et al.* (HAB)⁽¹⁾ and, independently, Percus⁽²⁾ have considered the Ornstein–Zernike (OZ) equation for a fluid in contact with an impenetrable wall.⁴ Percus has considered the equation directly, while HAB

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⁴ The observation of this paper that the wall–particle problem can be treated using standard Wiener–Hopf techniques was independently made by Percus in his work, which came to our attention too late to be compared to, or incorporated into, our own results here.

have shown how it can be deduced from the limiting case of a mixture in which one of the components (which we will label 0) grows in size and diminishes in concentration in such a manner that the bulk properties of the fluid remain unchanged. If the density of this component is ρ_0 and the exclusion diameter is σ_0 , this limit amounts to

$$\sigma_0 \rightarrow \infty \quad (1)$$

$$\rho_0 \sigma_0^3 \rightarrow 0 \quad (2)$$

HAB⁽¹⁾ further showed that the OZ equation can be written

$$h_0(x) = c_0(x) + 2\pi\rho_B \int_0^\infty dt \int_{x-t}^{x+t} ds t c_B(t) h_0(s) \quad (3)$$

where

$$h_0(x) = g_0(x) - 1$$

and $g_0(x)$ is the wall-particle distribution function for the solute or bulk particles and the wall. In other words, if ρ_B is the bulk numerical density, then $\rho_B g_0(x)$ gives the probability of finding a center of a bulk molecule at a distance x from the surface of the hard wall.

Similarly, $c_0(x)$ is the direct correlation function for the wall-bulk molecule system and $c_B(t)$ is the direct correlation function for the bulk molecules in the absence of the wall. In considering (1) and (2), it is assumed that the mixture is already in its thermodynamic limit (i.e., in an infinite volume) and is of uniform expected density. That is, each particle—including the arbitrarily large particle that becomes a wall—is equally likely to be centered at any point in the infinite volume. The system described by $c_B(t)$ is likewise an infinite and uniform system.

In their work, HAB⁽¹⁾ obtained the solution of (3) for $h_0(x)$ in a system of a hard-sphere fluid in contact with a hard wall, using the Percus-Yevick approximation for $c_0(x)$ as well as $c_B(t)$. A solution for the more generally relevant case in which the wall and the bulk hard spheres interact attractively, with an exponential $c_0(x)$ for $x > \sigma/2$, has been subsequently obtained by Waisman *et al.*⁽³⁾

It is the purpose of the present work to show that (3) and its extension to a multicomponent mixture have a solution for a class of approximate $c_0(x)$ and $c_B(t)$ of physical and physicochemical interest. In order to make this statement more precise, let us divide the wall-bulk correlation function $c_0(x)$ into two parts,

$$c_0(x) = c_0^0(x) - \phi(x) \quad (4)$$

where $c_0^0(x)$ is 0 for $x > \sigma/2$ and is an unknown function for $x \leq \sigma/2$. The $\phi(x)$, assumed zero for $x \leq \sigma/2$, will be called the “wall–particle closure function” of the OZ equation. In general, there are two different types of closure that one can contemplate on the two-point level, whether one is considering the wall–particle direct correlation function $c_0(x)$ or the particle–particle direct correlation function $c_B(t)$:

(i) An approximate direct correlation function can be explicitly prescribed in functional form, as in the case of the mean spherical⁽⁴⁾ (MS) and generalized mean spherical⁽⁵⁾ (GMS) approximations.

(ii) The direct correlation functions can be given instead as a functional of the total correlation function and the interaction potential, as in the case of the Percus–Yevick (PY), hypernetted chain (HNC), and related approximations.⁽⁶⁾

We shall regard the $c_B(t)$ that appears in (3) as a known function, determined beforehand by means of the MS, PY, HNC, or some other approximation. For simplicity we shall further restrict ourselves here to the case of a $c_B(t)$ that falls off exponentially fast as $t \rightarrow \infty$, as in the MS or PY approximation when the interparticle potential itself so falls off. If $c_0(x)$ is obtained from a wall–particle closure of type (i), $\phi(x)$ is also a prescribed function. In this case we can then give a closed-form solution to (3) as long as the Fourier transform of $\phi(x)$, $\tilde{\phi}(k)$, is a meromorphic function with no essential singularities in the lower complex k plane. If $c_0(x)$ is instead obtained from a wall–particle closure of type (ii), we lose the explicit form of the solution, but we can still reduce Eq. (3) to a simpler integral equation, the degree of simplicity depending upon the closure used. For the wall–particle functions, the PY closure is

$$-\phi(x) = [h(x) + 1][1 - e^{+\beta w(x)}] \quad \text{for } x > \sigma/2 \quad (5)$$

where $w(x)$ is the wall–particle potential, while the HNC closure is

$$-\phi(x) = h(x) - \ln[h(x) + 1] - \beta w(x) \quad (6)$$

The MS closure is simply

$$\phi(x) = \beta w(x) \quad (7)$$

while the simplest form of GMS closure is

$$\phi(x) = A(\rho, \beta)w(x) \quad (8)$$

with $A(\rho, \beta)$ suitably adjusted⁽⁵⁾ to improve thermodynamic self-consistency of the approximation.

2. FORMAL SOLUTION

We consider a multicomponent fluid in which all the particles are spherical and are labeled 1, 2, ..., n . For such a system the natural generalization of Eq. (3) is

$$h_{0i}(x) = c_{0i}(x) + 2\pi \sum_j \rho_j \int_0^\infty dt \int_{x-t}^{x+t} ds t c_{ij}(t) h_{0j}(s) \quad (9)$$

where $h_{0i}(x) = g_{0i}(x) - 1$ is the correlation function for the wall-component i pair, $c_{0i}(x)$ is the direct correlation function for the same pair, ρ_j is the bulk density of component j , and $c_{ij}(t)$ is the direct correlation function for the i, j pair. Consider now the Fourier transform of Eq. (9). For this purpose define

$$\tilde{h}_{0i}(k) = \int_{-\infty}^{\infty} dx e^{ikx} h_{0i}(x) \quad (10)$$

Also, we divide c_{0i} into two parts [(4)]

$$c_{0i}(x) = c_{0i}^0(x) - \phi_i(x) \quad (11)$$

so that

$$c_{0i}^0(x) = 0 \quad \text{for } x \geq \sigma_i/2 \quad (12)$$

and

$$\phi_i(x) = 0 \quad \text{for } x < \sigma_i/2 \quad (13)$$

where σ_i is the hard-core diameter of molecule i . The Fourier transforms of these quantities are then

$$\tilde{c}_{0i}^0(k) = \int_{-\infty}^{\sigma_i/2} dx e^{ikx} c_{0i}^0(x) \quad (14)$$

$$\tilde{\phi}_i(k) = \int_{\sigma_i/2}^{\infty} dx e^{ikx} \phi_i(x) \quad (15)$$

We also define

$$\tilde{c}_{ij}(k) = (4\pi/k) \int_0^\infty dr r (\sin kr) c_{ij}(r) \quad (16)$$

and then have

$$\sum_{l=1}^n \tilde{h}_{0l}(k) [\delta_{lj} - \rho_l \tilde{c}_{lj}(k)] = \tilde{c}_{0j}^0(k) - \tilde{\phi}_j(k) \quad (17a)$$

or in matrix form

$$\tilde{\mathbf{h}}_0 [\mathbf{I} - \rho \tilde{\mathbf{c}}(k)] = \tilde{\mathbf{c}}_0^0(k) - \tilde{\mathbf{\phi}}(k) \quad (17b)$$

where $\tilde{\mathbf{h}}_0$, $\tilde{\mathbf{c}}_0^0$, and $\tilde{\mathbf{\phi}}$ are row vectors, while $\mathbf{I} - \rho \tilde{\mathbf{c}}(k)$ is an n by n square matrix.

Now, it can be shown⁽⁷⁾ that for fluid systems such that $c_{ij}(t)$ satisfies certain conditions, to which we return at the end of this section, we have

$$\mathbf{I} - \rho \tilde{\mathbf{c}}(k) = \tilde{\mathbf{Q}}(k) \tilde{\mathbf{Q}}^T(-k) \tag{18}$$

where the matrix $\tilde{\mathbf{Q}}(k)$ is bounded and nonsingular in the upper half complex k plane, while the matrix $\tilde{\mathbf{Q}}^T(-k)$ is bounded and nonsingular in the lower half complex k plane. Furthermore, the matrix $\tilde{\mathbf{Q}}(k)$ has to be of the form

$$\tilde{Q}_{ij}(k) = \delta_{ij} - \rho_j \int_{\lambda_{ji}}^{\infty} dr e^{ikr} Q_{ij}(r) \tag{19}$$

where

$$\lambda_{ji} = \frac{1}{2}(\sigma_j - \sigma_i)$$

From (10) and (11) we get at once

$$\tilde{\mathbf{h}}_0(k) \tilde{\mathbf{Q}}(k) = \{\tilde{\mathbf{c}}_0^0(k) - \tilde{\Phi}(k)\} \{\tilde{\mathbf{Q}}^T(-k)\}^{-1} \tag{20}$$

Consider now the Fourier inverse of this equation for $x > \sigma_i/2$, $\delta > 0$,

$$\begin{aligned} \frac{1}{2\pi} \int_{-\infty - i\delta}^{\infty - i\delta} dk e^{-ikx} \sum_j \tilde{h}_{0j}(k) \tilde{Q}_{ji}(k) &= \frac{1}{2\pi} \int_{-\infty - i\delta}^{\infty - i\delta} dk e^{-ikx} \sum_j \tilde{c}_{0j}^0(k) \{\tilde{\mathbf{Q}}^T(-k)\}_{ji}^{-1} \\ &\quad - \frac{1}{2\pi} \int_{-\infty - i\delta}^{\infty - i\delta} dk e^{-ikx} \sum_j \tilde{\phi}_j(k) \{\tilde{\mathbf{Q}}^T(-k)\}_{ji}^{-1} \end{aligned} \tag{21}$$

We seek solutions such that the function $\tilde{c}_{0j}^0(k)$ is bounded and has no singularities in the complex half-plane, $\text{Im } k < \delta$. Furthermore, $\tilde{\mathbf{Q}}^T(-k)$ is nonsingular in that region. More precisely we require for $k = -iy$, $y \rightarrow \infty$,

$$\tilde{c}_{0j}^0(-iy) \sim e^{y\sigma_j/2} \tag{22}$$

while we know that

$$\{\tilde{\mathbf{Q}}^T(iy)\}_{ji}^{-1} \sim e^{y\lambda_{ij}} \tag{23}$$

Therefore the integrand of the first term in the right-hand side of (21) is bounded by $M e^{y(\sigma_i/2 - x)}$. For $x > \sigma_i/2$ we can close a contour around the lower k plane, and this term will have no contribution. This eliminates the unknown $\tilde{c}_{0j}^0(x)$ and is the crux of our solution. The result of (21) is then, for $x > \sigma_j/2$, $\delta \rightarrow 0$,

$$\begin{aligned} h_{0j}(x) - \sum_l \rho_l \int_{\lambda_{jl}}^{\infty} dr h_{0l}(x - r) Q_{lj}(r) \\ = -\frac{1}{2\pi} \int_{-\infty}^{\infty} dk \sum_l \tilde{\phi}_l(k) \{\tilde{\mathbf{Q}}^T(-k)\}_{lj}^{-1} e^{-ikx} \end{aligned} \tag{24}$$

$$= -\sum_l \int_{\sigma_l/2}^{\infty} dy \phi_l(y) P_{lj}(y - x) \tag{25}$$

where the last identity was obtained from Parseval's relation upon introducing the function

$$P_{ij}(z) = (1/2\pi) \int_{-\infty}^{\infty} dk e^{ikz} \{\tilde{\mathbf{Q}}^T(-k)\}_{ij}^{-1} \tag{26}$$

Equations (24) and (25) are the formal solution of the stated problem. However, to obtain quantities of thermodynamic or structural interest we must go further. We can not in general get $h_{0j}(x)$ for arbitrary x in closed form, but we can get the contact value $h_{0j}(\sigma_j/2)$, the Laplace transform, and the total excess surface concentration in a rather simple way. The contact value has direct interest since it represents the adsorption probability and partial pressure.

Notice that in the second term of the left-hand side of (24), for $x = \sigma_j/2$, the argument of $h_{0i}(x - r)$ is less than $\sigma_i/2$. Therefore, since the hard-core condition implies

$$h_{0i}(y) = -1, \quad y < \sigma_i/2 \tag{27}$$

we have

$$\begin{aligned} h_{0j}(\sigma_j/2) &= -\sum_l \rho_l \int_{\lambda_{jl}}^{\infty} dr Q_{lj}(r) \\ &\quad - (1/2\pi) \int_{-\infty}^{\infty} dk e^{-ik\sigma_j/2} \sum_l \tilde{\phi}_l(k) \{\tilde{\mathbf{Q}}^T(-k)\}_{lj}^{-1} \end{aligned} \tag{28}$$

or

$$\begin{aligned} h_{0j}(\sigma_j/2) &= -\sum_l \left\{ \rho_l \int_{\lambda_{jl}}^{\infty} dr Q_{lj}(r) \right. \\ &\quad \left. + \int_{\sigma_l/2}^{\infty} dy \phi_l(y) P_{lj}(y - \sigma_j/2) \right\} \end{aligned} \tag{29}$$

The Laplace transform is also quite straightforward, and is given by

$$\begin{aligned} \tilde{g}_{0i}(s) &= \sum_{i,j} e^{-s\sigma_j/2} \left\{ \frac{1}{s} \tilde{Q}_{ij}(0) - \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \frac{e^{-ik\sigma_j/2}}{s + ik} \tilde{\phi}_{0i}(k) [\tilde{\mathbf{Q}}^T(-k)]_{ij}^{-1} \right\} \\ &\quad \times \{\tilde{\mathbf{Q}}(is)\}_{ji}^{-1} \end{aligned} \tag{30}$$

where

$$\tilde{g}_{0i} = \int_0^{\infty} dx e^{-sx} [h_{0i}(x) + 1] = \int_0^{\infty} dx e^{-sx} g_{0i}(x) \tag{31}$$

The Laplace inversion of (30) will yield a "zone-by-zone" representation of the physically interesting quantity $g_{0i}(x)$, which will be at its simplest in the

first zone $\sigma/2 < x < 3\sigma/2$. [We recall that $\rho_i g_{oi}(x)$ is the numerical density of component i at a distance x from the hard surface.]

Finally, we can calculate the total excess density of a component near the wall

$$\rho_i \int_0^\infty dx (g_{oi} - 1) = \lim_{s \rightarrow 0} \rho_i \left[\tilde{g}_{oi}(s) - \frac{1}{s} \right] \tag{32}$$

In the simple case of hard walls in the Percus–Yevick approximation, $\tilde{\phi}_{oi}(k) = 0$.

We return to the conditions under which (18) is valid. Baxter^{(7),5} explicitly considered (18) only for $c_{ij}(t)$ that vanish identically for large t . However, his results generalize to the case of exponentially decaying $c_{ij}(t)$.

3. MEAN SPHERICAL AND RELATED CLOSURES

The results of the preceding section are closed-form equations only for closure functions $\phi_{oi}(x)$ that are of prescribed functional form. This is the case in the mean spherical and generalized mean spherical approximations.^(4,5)

The problem is essentially solved if we know the right-hand side of (24), (25), or (30). Because of the analytic properties of $\tilde{\mathbf{Q}}^T(-k)$, which is non-singular and bounded in the lower half complex k plane, we can close a contour around it. Suppose that the poles of $\tilde{\phi}_i(k)$ in the lower half-plane are located at

$$k = z_m, \quad m = 1, 2, \dots \tag{33}$$

We get from (24) (with Res denoting the residue of a term)

$$\begin{aligned} h_{oj}(x) - \sum_i \rho_i \int_{\lambda_{ji}}^\infty dr h_{oi}(x-r) Q_{ij}(r) \\ = i \sum_{i,m} \text{Res } \tilde{\phi}_i(k) \{ \tilde{\mathbf{Q}}^T(-k) \}_{ij}^{-1} e^{-ikx} \Big|_{k \rightarrow z_m} \end{aligned} \tag{34}$$

We shall apply this to the Yukawa potential, which is of intrinsic interest, and can also be used as an approximate “image potential” between ions and a metallic grounded electrode,⁽⁹⁾

$$u_j(x) = -\frac{e^2 z_j^2}{2\epsilon_0} \frac{e^{-\Gamma x}}{x} \tag{35}$$

where e is the electron charge, z_j is the electrovalence of ion j , ϵ_0 is the dielectric constant of the medium, and Γ^{-1} is four times the shielding length that depends on the ionic strength of the solution.^(7,10)

⁵ See Ref. 8 for the one-species case.

In the MS approximation

$$\phi_j(x) = +\beta u_j = +A_j e^{-\Gamma x}/x \quad (36)$$

$$A_j = -\beta e^2 z_j^2 / 2\epsilon_0 \quad (37)$$

For this case, Eq. (9) yields

$$\begin{aligned} h_{0j}(x) &= \sum_l \rho_l \int_{\lambda_{jl}}^{\infty} dr h_{0l}(x-r) Q_{lj}(r) \\ &= -\sum_l A_l \int_{\sigma_{l/2}}^{\infty} dy \frac{e^{-\Gamma y}}{y} P_{lj}(y-x) \end{aligned} \quad (38)$$

The last integral will have to be evaluated numerically. A physically interesting quantity is the adsorption isotherm, given by (29), in slightly different form

$$g_{0j}(\sigma_j/2) = \sum_l \left[\tilde{Q}_{lj}(0) - A_l \int_{\sigma_{l/2}}^{\infty} dy (e^{-\Gamma y}/y) P_{lj}(y - \frac{1}{2}\sigma_j) \right] \quad (39)$$

Due to the intrinsic weakness of the MS approximation, we expect that the exponential approximation⁽¹¹⁾ should give a substantially better theory. The exponential approximation is obtained simply by exponentiating (39). Thus

$$g_{0j}^{\text{exp}}(\sigma_j/2) = [g_{0j}^{\text{HC}}(\sigma_j/2)] \exp \left\{ -\sum_l A_l \int_{\sigma_{l/2}}^{\infty} dy (e^{-\Gamma y}/y) P_{lj}(y - \frac{1}{2}\sigma_j) \right\} \quad (40)$$

where $g_{0j}^{\text{HC}}(\sigma_j/2)$ is the hard-core contact value, which in the Percus–Yevick approximation is, according to the result of HAB,⁽¹⁾

$$g_{0j}^{\text{HC}}(\sigma_j/2) = \sum_l \tilde{Q}_{lj}(0) \quad (41)$$

As can be seen from (40) and (37), there is a positive adsorption caused by the image-force attraction that is proportional to A_j , and thus to the square of the charge z_j . A full discussion of this equation is left for the future.

4. EXTENSIONS

Although uniform in the sense described in our introduction, our system is not uniform with respect to the wall that we have introduced by taking the limit (1)–(2). In fact, relative to that wall, the one-particle density function $\rho_i(\mathbf{r})$ of species i is related to the $h_{0i}(x)$ of Eq. (9) by the expression

$$\rho_i(\mathbf{r}) = \rho_i [h_{0i}(x) + 1] \quad (42)$$

where \mathbf{r} is a vector with Cartesian coordinates (x, y, z) .

We note that the closure schemes (5)–(8) and their generalizations to the case of a fluid of many components can easily be embedded in expansions⁶

⁶ Various forms of these exact expansions are summarized in Ref. 12.

that constitute a formally exact theory when appended to (9). The same expansion techniques that provide the basis for theories of $c_{ij}(t)$ are of value in dealing with $c_{0i}(x)$ as well. For example, one can replace (5)–(8) by an exact series representation that gives $c_0(x) + \beta w(x)$ as a functional of $h(x)$, ρ_B , and $h_B(t)$, where $h_B(t)$ is the bulk two-particle total correlation function. This series follows immediately from the general h -bond ρ -vertex expansion^(6,12) of $c(\mathbf{r}_0, \mathbf{r}_i) + \beta w(\mathbf{r}_0, \mathbf{r}_i)$ upon making the particle at \mathbf{r}_0 a wall, where $w(\mathbf{r}_0, \mathbf{r})$ is the two-point potential that becomes $\beta w(x)$, and $c(\mathbf{r}_0, \mathbf{r})$ is the two-point direct correlation function that becomes $c_0(x)$. For some purposes it is more useful to employ a functional Taylor-series representation,^(13,14) such as Eqs. (4)–(5) of Ref. 13, which yield a representation of $\phi(x)$ in terms of $h(x)$, ρ_B , the bulk chemical potential $\mu(\rho, \beta)$, and $\hat{c}(\mathbf{r}_i, \mathbf{r}_j)$ and its functional derivatives with respect to the one-particle distribution function $\rho(\mathbf{r})$, where $\hat{c}(\mathbf{r}_i, \mathbf{r}_j) = c(\mathbf{r}_i, \mathbf{r}_j) - \delta(\mathbf{r}_i, \mathbf{r}_j)/\rho(\mathbf{r}_i)$. We introduce the notation

$$c_B(1, \dots, m)_{\rho(x)} = \left. \frac{\delta^{m-2} \hat{c}(\mathbf{r}_1, \mathbf{r}_2)}{\delta \rho(\mathbf{r}_3) \dots \delta \rho(\mathbf{r}_m)} \right|_{\rho(\mathbf{r}_i) = \rho(x)} \quad (43)$$

so that $\hat{c}_B(1, 2)_{\rho(x)}$ stands for $c_B(t_{12}) - \delta(\mathbf{r}_1, \mathbf{r}_2)/\rho$ evaluated with ρ set equal to $\rho(x) = \rho_B[h_0(x) + 1]$, $\hat{c}_B(123)_{\rho(x)}$ stands for its functional derivative with respect to $\rho(\mathbf{r}_3)$ evaluated at $\rho(x)$, etc. Similarly we let $\mu_{\rho(x)}$ stand for $\mu(\rho, \beta)$ evaluated with $\rho = \rho(x)$. When the distinguished particle 1 of Eqs. (4) and (5) of Ref. 13 (the particle 0 here) becomes a wall, those equations become

$$c_0(x) = -\beta w(x) - \beta[\mu_{\rho(x)} - \mu - \rho_B h_0(x) \partial \mu / \partial \rho] + S_1(x) + \sum_{n \geq 2} S_n(x) \quad (44a)$$

where

$$S_1(x) = \rho_B \int [h_0(x_2) - h_0(x)] [\hat{c}_B(1, 2)_{\rho(x)} - \hat{c}_B(1, 2)] d\mathbf{r}_2 \quad (44b)$$

and for $n \geq 2$,

$$S_n(x) = \frac{\rho_B^n}{n!} \int \prod_{i=2}^{n+1} [h_0(x_i) - h_0(x)] \hat{c}_B(1, \dots, n+1)_{\rho(x)} d\mathbf{r}_2 \dots d\mathbf{r}_{n+1} \quad (44c)$$

In (44) we have omitted the subscript 1 on the Cartesian coordinate x of \mathbf{r}_1 for notational simplicity.

For a long-ranged $h_0(x)$ [e.g., for $w(x) \rightarrow x^{-n}$, $n > 3$] and a short-ranged $c_B(1, \dots, n)$ (e.g., for hard spheres) one can expect rapid convergence of (44), with the behavior of $c_0(x) + \beta w(x)$ dominated by the

$$-\beta[\mu_{\rho(x)} - \mu - \rho_B h_0(x) \partial \mu / \partial \rho]$$

so that as $x \rightarrow \infty$,

$$\beta w(x) - \phi(x) \rightarrow \frac{\rho_B^2}{2} \frac{\partial^2 \beta \mu}{\partial \rho^2} h_0^2(x) \quad (45)$$

For small x , and for other combinations of wall-particle and particle-particle potentials, the convergence of (44) remains to be studied.

The HNC and PY approximations (5) and (6) can be systematically corrected using the same techniques.⁽¹⁴⁾ Let us write $-\beta\mu$ as m , so that (44) can be expressed as

$$-\phi(x) = -\phi(x)^{\text{MSA}} + m_{\rho(x)} - m - h_0(x) \frac{\partial m}{\partial \rho} + \sum_{n \geq 1} S_n^{\text{HNC}}(x) \quad (46)$$

One finds analogously

$$-\phi(x) = -\phi(x)^{\text{HNC}} + l_{\rho(x)} - l - h_0(x) \frac{\partial l}{\partial \rho} + \sum_{n \geq 1} S_n^{\text{HNC}}(x) \quad (47)$$

where $l = \ln \rho - \beta\mu$, and the S_n^{HNC} have the same structure as the S_n^{MSA} , except with $\hat{c}_B(1, \dots, m)$, $m \geq 2$, replaced throughout by

$$c_B(1, \dots, m) = \frac{\delta^{m-2} c(\mathbf{r}_1, \mathbf{r}_2)}{\delta \rho(\mathbf{r}_3) \cdots \delta \rho(\mathbf{r}_m)}$$

Due to the factors $h_0(x_i) - h_0(x)$ in the integrands, S_n^{MSA} and S_n^{HNC} are in fact identical functions of x . [The resulting identity $\sum_{n \geq 1} S_n^{\text{MSA}} = \sum_{n \geq 1} S_n^{\text{HNC}}$ can also be verified directly by equating (46) and (47).] One similarly finds

$$-R\phi(x) = -R\phi^{\text{PY}}(x) + R_{\rho(x)} - R - h_0(x) \frac{\partial R}{\partial \rho} + \sum_{n \geq 1} S_n^{\text{PY}}(x) \quad (48)$$

where $R = \rho/\exp(\beta\mu)$. The S_n^{PY} also retains the structure of the S_n^{MSA} , except with the \hat{c}_B now replaced by $\rho(\mathbf{r}_1)c(\mathbf{r}_1, \mathbf{r}_2)/z(\mathbf{r}_1)$ and its derivatives with respect to $\rho(\mathbf{r}_1)$, where $z(\mathbf{r}) = \exp[\beta\mu - \beta w(\mathbf{r}_0, r)]$. The $S_n^{\text{PY}}(x)$ are different functions than the $S_n^{\text{MSA}}(x)$. The relative rates of convergence of (48) and (44) will depend on the details of the wall-particle and interparticle potentials.

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